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GHGT-12

The application of noble gases and carbon stable isotopes in tracing the fate, migration and storage of CO₂

Stuart Gilfillan^a, Stuart Haszedline^a, Fin Stuart^b, Domokos Gyore^b, Rachel Kilgallon^a,
Mark Wilkinson^{a*}

^a*School of GeoSciences, University of Edinburgh, Edinburgh, EH9 3JW, Scotland, UK*

^b*Isotope Geoscience Unit, Scottish Universities Environmental Research Centre (SUERC), University of Glasgow, East Kilbride, G75 0QF, Scotland, UK*

Abstract

The noble gases (He, Ne, Ar, Kr and Xe) are present in trace quantities in all natural and engineered CO₂. They have proved to be extremely powerful tracers of both the CO₂ source, and when combined with carbon stable isotopes, the subsurface processes that control the fate of CO₂. Here we present a summary of the progress made over the past decade in using noble gases and stable carbon isotope tracing techniques in CO₂ storage studies. We outline the initial lessons which were learnt from the study of natural CO₂ reservoirs, then show the recent progress that has been made in tracing CO₂ injected into a CO₂-EOR field. We show the application of noble gases in determining natural CO₂ leakage to the shallow groundwater and their use in successfully refuting the allegations of CO₂ leakage made at the Weyburn CO₂-EOR project. Our results illustrate that good progress has been made in using noble gases to determine both the short-term and long-term fate of CO₂ in the subsurface and in the determination of the extent of groundwater interaction that the injected CO₂ has undergone. However, there are still outstanding questions, particularly regarding the exact behaviour of the noble gases compared to CO₂ and we show preliminary results from a laboratory study to investigate how noble gas transport through real rock compares to that of CO₂.

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* Corresponding author. Tel.: +44 131 651 3462.
E-mail address: stuart.gilfillan@ed.ac.uk

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1. Introduction

The noble gases (He, Ne, Ar, Kr and Xe) are present in trace quantities in all natural and engineered CO₂. There are three distinct sources of noble gases in subsurface fluids (crust, mantle and atmosphere) which are isotopically distinct. Further, they are inert and are not affected by chemical reactions in the reservoir. Consequently the noble gases are extremely powerful tracers of both the CO₂ source and of the subsurface processes that act on CO₂. They have been widely used to trace regional groundwater flow [1, 2] and several studies have successfully demonstrated the potential of noble gases to trace the origins of CO₂ and its fate within reservoirs [3-6].

2. Determining the mechanisms of CO₂ storage in natural CO₂ reservoirs

Noble gas measurements in CO₂ have been used previously to determine that the CO₂ contained within five natural CO₂ reservoirs from the Colorado and Rocky Mountain provinces contained mantle derived CO₂ [6]. This conclusion was based on the high concentration of mantle derived ³He within the CO₂ reservoirs which resulted in CO₂/³He ratios within the magmatic range of $1 \times 10^9 - 1 \times 10^{10}$ [7]. Recent work has shown that nine natural CO₂ reservoirs from around the globe show a clear, and quite amazing, correlation between decreasing CO₂/³He and increasing formation water derived noble gases ²⁰Ne, and crustal derived but groundwater transported ⁴He (Fig. 1) [3]. As the noble gases are conservative, the change in CO₂/³He is due to CO₂ loss and this is quantitatively related to the volume of formation water ‘seen’ by the gas.

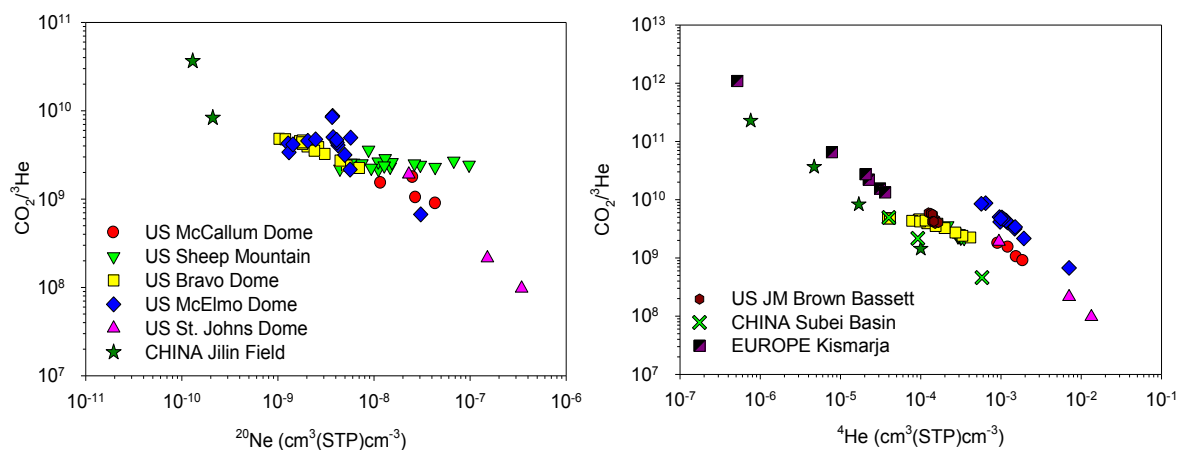


Fig. 1a. Left - CO₂/³He variation plotted against ²⁰Ne in samples from the ‘global’ data set of CO₂-rich natural gas fields. There is a general trend in this data set of decreasing CO₂/³He with increasing ²⁰Ne. ³He is conservative within the gas phase. Variations in CO₂/³He therefore represent subsurface changes in CO₂ concentration in the emplaced CO₂ phase. Since the only subsurface source of the ²⁰Ne now in the CO₂ phase is the formation water, the CO₂ sink must be linked to the formation water contacted by the gas phase.

Fig. 1b. Right - The ‘global’ data sets of CO₂ gas fields also show a strong correlation between decreasing CO₂/³He and increasing ⁴He concentration. ⁴He accumulates in formation water over time and underscores the importance of formation water in controlling the mechanism of subsurface CO₂ removal.

Using a combination of the noble gases and carbon stable isotopes it is also possible to differentiate between the amount of CO₂ stored as carbonate mineral precipitate and the amount dissolved in the reservoir formation water. This is because there is a distinct difference between the stable carbon isotopic fractionation which occurs when CO₂ gas dissolves into water and that which occurs when carbonate precipitate is formed [8]. Out of the nine reservoirs studied, only two of them required carbonate precipitation to have occurred to account for the dataset [3].

The Bravo Dome reservoir required the greatest portion of CO₂ precipitation. The carbon stable isotope values exhibit evidence for the maximum amount of carbonate precipitation to be 18% of the total CO₂ volume lost relative to ³He (Fig. 2a). This is minor in comparison to the 40% of CO₂ that was also dissolved to the formation water within the field (Fig. 2a). The datasets from the other seven fields can all be explained by dissolution of CO₂ into the formation water within a pH range of 5-6. The dissolution trend exhibited by these fields also allows determination of the reservoir pH conditions under which CO₂ dissolution is occurring. This is due to the different carbon stable isotope fractionation factors that result from CO₂(g) dissolving either to HCO₃⁻ and H₂CO₃ [8].

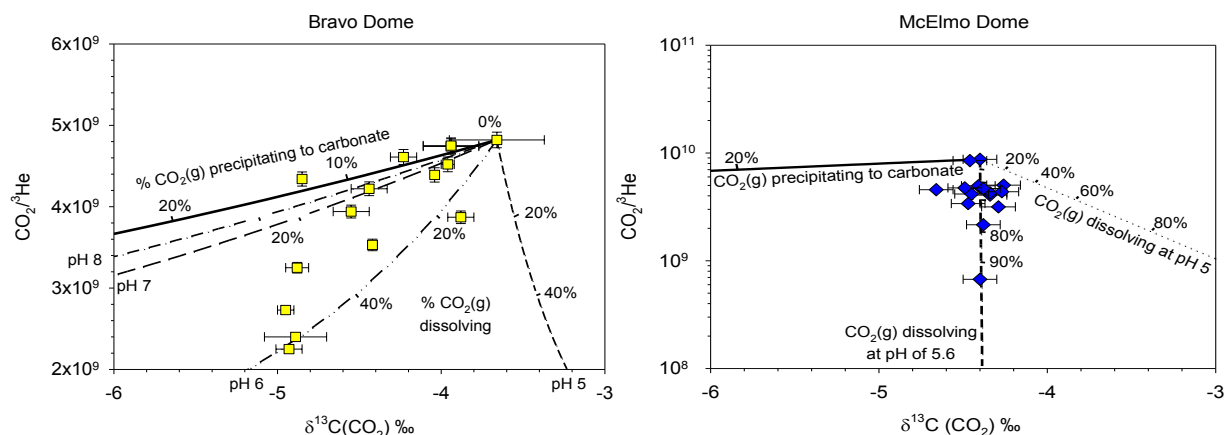


Fig. 2a. Left - $\delta^{13}\text{C}(\text{CO}_2)$ against $\text{CO}_2/{}^3\text{He}$ for Bravo Dome. The solid line shows the predicted trend for carbonate mineral precipitation and the dashed lines show dissolution trends for varying formation water pH. Bravo Dome data is not consistent with the major CO₂ sink being precipitation of carbonate.

Fig. 2b. Right - $\delta^{13}\text{C}(\text{CO}_2)$ against $\text{CO}_2/{}^3\text{He}$ for McElmo Dome. Invariant $\delta^{13}\text{C}(\text{CO}_2)$ with over an order of magnitude change in $\text{CO}_2/{}^3\text{He}$ cannot be accounted for by precipitation (solid line). Dissolution of reservoir CO₂ into formation water at pH=5.6 would produce the observed results.

3. Tracing the migration and fate of CO₂ in the Cranfield EOR reservoir, Mississippi

3.1. Cranfield CO₂-EOR field background and sampling history

The Cranfield CO₂-EOR field is located in southwest Mississippi, ~20 km east of Natchez. The reservoir was discovered in 1943 and oil and gas production first commenced in 1944. The field consists of a simple dome structure, with a gas cap and associated down-dip oil ring. Pressure maintenance was achieved by gas recycling until the gas cap was depleted in 1959. It was subsequently abandoned in 1966 after unsuccessful water injection tests in 1958-59. The field was re-entered for CO₂ injection for EOR in July 2008 by Denbury Resources Inc. Prior to injection the reservoir re-equilibrated to hydrostatic pressure by groundwater infiltration after abandonment. Continuous CO₂ injection without water injection means that Cranfield can be considered as an analogue for injection into a saline aquifer. This is significant as saline formations offer the vast majority of available global CO₂ storage capacity [9-11].

The CO₂ injected into the Cranfield oil field for EOR is sourced from the Jackson Dome natural CO₂ reservoir, located to the northeast of Jackson, MS. The CO₂ contained in Jackson Dome is sourced from the mantle [12] and has a mantle rich noble gas fingerprint. The Jackson Dome CO₂ is piped to Cranfield via a 400km long high pressure CO₂ pipeline. At Cranfield CO₂ and methane is separated from the produced gas and oil, and mixed with incoming Jackson Dome CO₂ and re-injected [13]. The amount of produced gas being recycled into the field has increased significantly with time. Between July 2009 and January 2013 the proportion of recycled gas increased from ~9 to ~30 % of the total injected gas [10]. In April 2010 the CO₂ injection rate reached one million metric tonnes per annum, and by January 2013 6.8 million metric tonnes of CO₂ had been injected, of which 4 million had

been retained in the reservoir [10, 14].

Sampling of the produced and injected gases from the Cranfield CO₂-EOR field was undertaken in 2009 and 2012. In 2009, 9 production wells and an injection well (containing a mixture of Jackson Dome CO₂ and gas recycled from the oil field) were sampled. In 2012, the 9 production wells sampled in 2009 were resampled along with an additional 3 wells which had been drilled between 2009 and 2012, and the same injection well which had been sampled in 2009. Additionally a sample of Jackson Dome CO₂ was taken from the pipeline supplying CO₂ to the Cranfield oil field prior to any mixing of this CO₂ with recycled gas from the field. All samples were collected at high-pressure wellheads. The CO₂ supply pipeline and injection wells were maintained at ~207 bar and ~32°C to keep CO₂ as a supercritical phase. The production wells produce oil, water and gas (comprised predominantly of CO₂ and CH₄) therefore samples were taken from the top of the flow line to avoid sampling liquid. Production wells were operating at pressures between ~8 and ~91 bar and ~62°C.

3.2. Results

The CO₂ piped from Jackson Dome to the Cranfield CO₂-EOR field is comprised almost entirely of CO₂ (99%) with a trace amount of CH₄ and noble gases making up the remainder. $\delta^{13}\text{C}_{\text{CO}_2}$ of this CO₂ is -2.9 ‰, the $^3\text{He}/^4\text{He}$ is 5.4 R_A (Fig. 3a) and $^{40}\text{Ar}/^{36}\text{Ar}$ is 4,268. These data are consistent with previous measurements made from samples collected at the Jackson Dome natural CO₂ field [12]. The injected gas sampled in 2009 and 2012 is significantly different from the Jackson Dome CO₂ composition piped to the field. The CO₂ content is lower; 96% (2009) and 87% (2012). $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ have also decreased over time (from 4.73 to 4.00 R_A and 2,909 to 2,723 respectively). These temporal changes are qualitatively consistent with the increased proportion of (methane-free) recycled production gas in the injected gas; ~9% in 2009 and ~30% in 2012 [10]. The $\delta^{13}\text{C}$ of the CO₂ injected in 2009 is -2.5 ‰ and -3.6 ‰ in 2012. There is no systematic change compared to Jackson Dome (-2.9 ‰), probably reflecting the variability in the isotopic composition of the recycled produced gas.

The produced gases show an increase in the proportion of injected gas with time. This is shown by a consistent increase in the concentration of CO₂ in the nine wells which were sampled in 2009 and 2012. The noble gas fingerprints in the produced gases become consistently closer to that of the injected gas over time, with increases in $^3\text{He}/^4\text{He}$, $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios and a decrease in ^4He , ^{20}Ne and ^{40}Ar concentrations (Fig. 3a). However, in our preliminary data there is no systematic change in the range of $\delta^{13}\text{C}_{\text{CO}_2}$ at these wells. In all cases $^4\text{He}/^{20}\text{Ne}$ are at least five orders of magnitude higher than the atmospheric value of 0.32 [15] immediately ruling out any contamination from atmosphere during sampling or analysis.

3.3. Tracing the fate of injected CO₂

3.3.1. Evidence for two component mixing - $^3\text{He}/^4\text{He}$ and CO₂ concentrations

The helium isotope data show clear two-component mixing. The majority of the data plot on modelled mixing curves (solid lines) between the mantle dominated injected gas and an in-situ crustal dominated natural gas end-member (using a $^3\text{He}/^4\text{He}$ of average crust of 0.02 R_A [16] and ^4He concentration of 165 ppm based on the average of the four samples with the lowest $^3\text{He}/^4\text{He}$ and CO₂ concentrations). However, five of the samples from 2009 do not plot on the mixing line between the in-situ crustal end member and the 2009 injected gas. All of these samples have CO₂ concentrations which are below 50%. These samples could be explained by either addition of an atmospheric air component with a $^3\text{He}/^4\text{He}$ ratio of 1 or loss of CO₂ relative to He. As the $^4\text{He}/^{20}\text{Ne}$ ratios are consistently five orders of magnitude higher than the atmospheric value, the addition of an atmospheric air component can be ruled out. Hence, these samples must have lost CO₂ relative to the noble gases.

3.3.2. Evidence for CO₂ loss - CO₂/ ^3He and CO₂ concentration

As outlined in Section 2 and in several previous studies, CO₂/ ^3He ratios have provided a useful means of

identifying the fate of CO₂ in natural CO₂ reservoirs. Hence, we investigated the relationship between CO₂/³He ratios and CO₂ concentration in the Cranfield produced gas samples. Figure 3b clearly shows that four of the five samples with low CO₂ concentrations also have correspondingly lower CO₂/³He ratios of between 4.02×10^8 to 1.24×10^9 , compared to the range of 3.15×10^9 to 4.15×10^9 exhibited by the remainder of the samples. The range of higher values is similar to that of the injected CO₂ of 2.77×10^9 . This clearly implies that the four samples which plot above the two component mixing lines in Fig 3a must have lost a proportion of the CO₂ component relative to ³He.

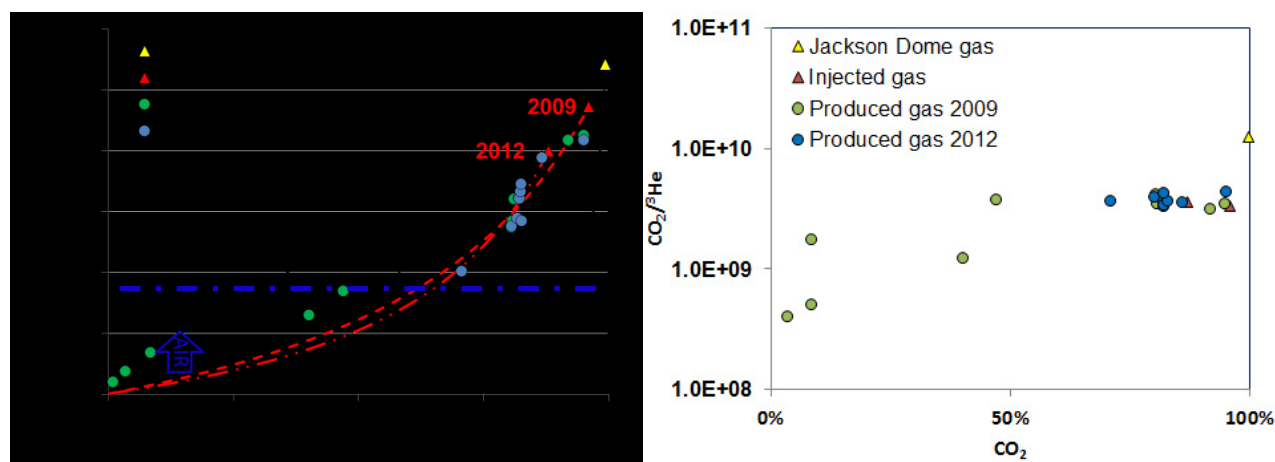


Fig. 3a. Left - ³He/⁴He against CO₂ for all Cranfield CO₂-EOR field samples. The dashed black line shows the two component mixing line for the piped Jackson Dome CO₂ mixing with a crustal end member with a ³He/⁴He ratio of 0.02 R_A. The two dashed red lines show the calculated 2 component mixing line for the gas injected into the Cranfield CO₂-EOR field in 2009 and 2012 mixing with the same crustal end member. The dashed blue line shows the atmospheric air ³He/⁴He ratio of 1R_A. It can be clearly seen that five of the 2009 samples do not plot on the mixing lines between the in-situ crustal end member and the two injected gas compositions.

Fig. 3b. Right - CO₂/³He against CO₂ concentration for all Cranfield CO₂-EOR field samples. It is clear that four of the five samples with low CO₂ concentrations also have correspondingly lower CO₂/³He ratios, compared to the consistently similar range to the injected gas exhibited by the remainder of the samples.

3.3.3. Evidence for CO₂ dissolution into the formation water - CO₂/³He, ²⁰Ne and ⁴He

As described earlier, natural CO₂ reservoirs show a strong correlation between decreasing CO₂/³He and increasing ²⁰Ne and ⁴He concentrations. Since the only subsurface source of ²⁰Ne in the CO₂ phase within natural CO₂ reservoirs is the formation water, the CO₂ sink must be linked to the formation water contacted by the gas phase. ⁴He accumulates in formation water over time and underscores the importance of formation water in controlling the mechanism of subsurface CO₂ removal and hence the increases in both ²⁰Ne and ⁴He corresponding to CO₂/³He decrease provides strong evidence of the dissolution of CO₂ into the formation water. Figure 4 shows that there is a clear increase in both ²⁰Ne and ⁴He concentrations in the four samples which show lower CO₂/³He ratios, compared to the majority of the produced gases and the injected gas. This is identical to the relationships observed in natural CO₂ reservoirs, which indicates that in the four samples in question, free phase CO₂ has been lost by dissolved into the formation water.

The majority of samples, however, have CO₂/³He within the average magmatic value similar as that of the gas injected into the Cranfield CO₂-EOR field. This indicates that minimal dissolution of CO₂ into the formation water has occurred in these samples. This suggests that the majority of injected CO₂ stays as a free phase and is physically/residually trapped. These preliminary results are the first that illustrate how well noble gas fingerprints are preserved in CO₂-EOR field and demonstrates how they help us identify and quantify CO₂ trapping mechanisms and interaction history in the reservoir.

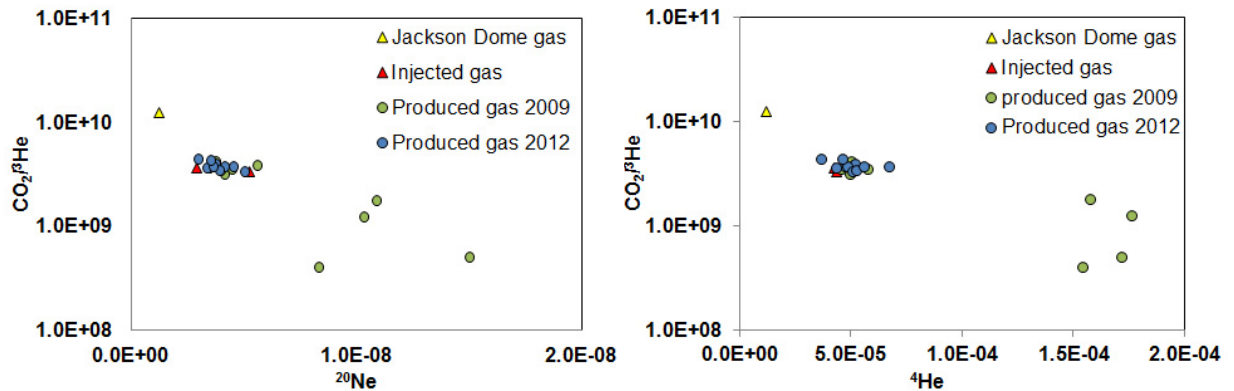


Fig. 4a. Left – $\text{CO}_2/{}^3\text{He}$ against ${}^{20}\text{Ne}$ for all Cranfield CO_2 -EOR field samples. There is an order of magnitude more ${}^{20}\text{Ne}$ in the 4 samples which show lower $\text{CO}_2/{}^3\text{He}$ ratios, which is strikingly similar to the relationship observed in natural CO_2 reservoirs and strong evidence for the loss of free phase CO_2 relative to ${}^3\text{He}$ as a result of CO_2 dissolution into the formation water.

Fig. 4b. Right - $\text{CO}_2/{}^3\text{He}$ against ${}^4\text{He}$ concentration for all Cranfield CO_2 -EOR field samples. Again the four samples with lower $\text{CO}_2/{}^3\text{He}$ ratios exhibit higher ${}^4\text{He}$ concentrations, similar to the relationship observed in natural CO_2 reservoirs and further evidence of the dissolution of CO_2 into the formation water, as being the sink of the free phase CO_2 lost relative to ${}^3\text{He}$.

4. Using Noble gases to identify and refute CO_2 leakage

4.1. Identifying natural CO_2 migration above the St. Johns Dome natural CO_2 reservoir

In addition to tracing both the migration and fate of CO_2 in natural CO_2 reservoirs, noble gases have proven to be powerful tracers of the natural migration of CO_2 to the surface above a natural CO_2 reservoir. Extensive travertine deposits surround the St. Johns Dome natural CO_2 reservoir, located on the border of Mid-Arizona/New Mexico, USA, highlighting a past history of migration of CO_2 rich fluids to the surface. Despite this historical evidence, no travertine formation is occurring at present and no gaseous CO_2 seeps are currently found in the area [17]. However, high concentrations of HCO_3^- are common in surface springs, shallow groundwater wells used for irrigation and deeper wells used to obtain cooling water for a coal fired power plant in the region. Previous chemical analysis of these waters implied a possible connection between the formation water within the CO_2 reservoir below and the HCO_3^- rich water in the near surface. This link was not found to be conclusive, due to significant differences in water types [17] and the fact that a soil gas survey surrounding these springs and wells was unable to differentiate additional CO_2 flux from that of background biological activity [18].

The production of radiogenic isotopes - such as ${}^4\text{He}$ and ${}^{40}\text{Ar}$ - by decay of U, Th and K in the local rocks presents a clear way of determining both the age of and original source of subsurface gases. Identification of significantly above atmospheric levels of ${}^4\text{He}$ were obtained from both groundwater wells and surface springs samples which directly overlay the natural CO_2 reservoir, implying the addition of a crustal component that had accumulated radiogenic ${}^4\text{He}$. Thus, a portion of the water originated at depth, having circulated in the crust for a significant period of time [19]. The ${}^4\text{He}$ excess was further illustrated by the significantly above air ${}^4\text{He}/{}^{20}\text{Ne}$ measured in all water samples, bar three springs which had low HCO_3^- values and were located significantly away from the CO_2 reservoir. Figure 5a shows that the majority of the surface spring waters and all of the groundwater well waters have ${}^3\text{He}/{}^4\text{He}$ ratios which are below the air ratio indicating that deep ${}^4\text{He}$ and deep CO_2 from the CO_2 field is present in the waters.

This clearly illustrated that the excess ${}^4\text{He}$ fingerprint entrained at depth was retained after migration of the waters to the surface. The simplest explanation is that the groundwater wells sampled shallow well and spring waters containing noble gases together with magmatic CO_2 derived from the deep reservoir. In this model, the high concentrations of HCO_3^- present in the sampled waters are then the direct result of the migration of dissolved CO_2

from the deep reservoir, illustrating for the first time that CO₂ can be fingerprinted from source to surface using noble gases, particularly He. Similar noble gas fingerprinting methods have also been recently used to detect the micro-seepage of CO₂ and CH₄ above the Teapot Dome oil field in Wyoming [20].

4.2. Refuting claims of CO₂ leakage above the Weyburn CO₂-EOR field

In January 2011 it was extensively reported that the Kerr family had been forced to move from their property located above the Weyburn-Midale Monitoring and Storage Project in Saskatchewan, Canada. A geochemical consultant from Petro-Find GeoChem Ltd., who was hired on behalf of the Kerr's, reported measurements of $\delta^{13}\text{C}$ (CO₂) isotope values in soil gases rich in CO₂ which were similar to those of the CO₂ injected into the deep oil reservoir [21]. The Petroleum Technology Research Centre (PTRC), who are responsible for the environmental monitoring of the Weyburn CO₂-EOR and storage operation, published a detailed response correctly stating that Petrofind had not taken the similar baseline $\delta^{13}\text{C}$ (CO₂) isotope measurements conducted prior to the injection into account [22]. Also as $\delta^{13}\text{C}$ (CO₂) is not a unique tracer, there were several other natural sources that could account for the measured values. Whilst this response went some way to addressing the public perception fears raised by the alleged CO₂ leakage claims, it was clear that more research was required to re-establish confidence in the safety and security of CO₂ stored at Weyburn. This was imperative for both the project itself and the future acceptance of the safety and security of CO₂ storage technologies. The International Performance Centre for Geologic Storage of CO₂ (IPAC-CO₂) undertook a detailed independent incident response protocol focused on the near surface soil gases, the noble gas composition of the shallow groundwaters and a hydrogeological analysis. In the following section we summarise the findings of the noble gas investigation.

In order to determine if migration of dissolved CO₂ from the Weyburn oil field was responsible for the alleged CO₂ anomaly, we completed noble gas measurements on water samples collected from four groundwater wells surrounding the Kerr quarter, near Goodwater in Saskatchewan. These were compared to the noble gas composition measured from fluids obtained from a production well and CO₂ and water obtained from two separate injection wells on the Weyburn-Midale oil field, located near to the Kerr quarter. The aim of the work was to test the hypothesis that migration of dissolved CO₂, originating from either the free phase CO₂ or water injected into the Weyburn-Midale oil field or from CO₂ contained in the produced fluids, was responsible for the CO₂ anomaly reported at the surface. This focused on dissolved CO₂ in the groundwaters as no free phase CO₂ was present in the sampled well waters and as recent research has shown that the sensitivity of He as a tracer is two orders of magnitude greater in groundwaters than in soil gases [20].

We observed no relationship between the $^3\text{He}/^4\text{He}$ ratio and HCO_3^- concentrations measured in the groundwaters from the Kerr site (Figure 5b). This is in stark contrast to the systematic relationship observed between HCO_3^- concentration and $^3\text{He}/^4\text{He}$ ratios in the St. Johns surface springs and groundwater wells (Section 4.1 and Figure 5b). In the Kerr groundwaters increased HCO_3^- , indicating increasing concentrations of dissolved CO₂ did not result in any variation in the air like $^3\text{He}/^4\text{He}$ ratios. There was also no relationship observed between $^3\text{He}/^4\text{He}$ ratios and the concentration of ^4He in the Kerr groundwaters. This strongly implied that there is no addition of deep crustal ^4He to the sampled waters surrounding the Kerr quarter and indicates that there was no migration of fluids from depth into the sampled wells. This was again in contrast to the clear relationship between decreasing $^3\text{He}/^4\text{He}$ and increasing ^4He concentrations observed in the St. Johns groundwaters.

All of the other noble gas (Ne, Ar, Kr) concentrations and the majority of noble gas ratios measured in the groundwaters from wells surrounding the Kerr quarter were within or very close to the air saturated values. We found no evidence in any of the noble gas data that there was any presence of deep crustal derived noble gases within the groundwaters surrounding the Kerr quarter, and hence no evidence of the migration of deep CO₂ from the Weyburn oil field into the groundwater on the Kerr quarter or the surrounding area.

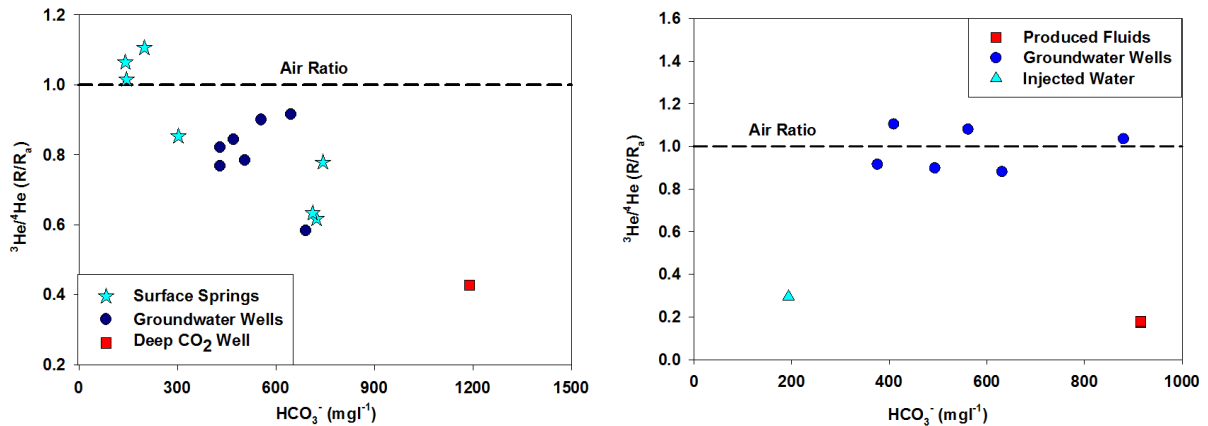


Fig. 5a (left) Plot of $^3\text{He}/^4\text{He}$ against HCO_3^- for waters sampled near to the natural St. Johns Dome CO₂ field, AZ. Here, the majority of the surface spring waters and all of the groundwater well waters have $^3\text{He}/^4\text{He}$ ratios which are below the air ratio indicating that deep ^4He and deep CO₂ from the CO₂ field is present.

Fig. 5b (right) Plot of $^3\text{He}/^4\text{He}$ against HCO_3^- concentration for samples collected at Weyburn. The shallow groundwaters sampled had air $^3\text{He}/^4\text{He}$, completely different to the CO₂ injected into the storage site or produced water. This shows that there was no CO₂ leakage to the groundwaters.

5. Comparing noble gas and CO₂ flow profiles through real rock

5.1. Introduction

Despite the good progress which has been made in using noble gases as tracers of CO₂ migration and fate there are still outstanding questions, particularly regarding the flow behavior of the noble gases compared to CO₂. Experimental work is underway at the University of Edinburgh to further constrain the factors and processes involved in noble gas and CO₂ transport. We are using unique experimental equipment to determine the factors affecting the transport of noble gases relative to CO₂. This work aims to investigate how noble gases could be used as effective early warning tracers of CO₂ migration in engineered CO₂ storage sites. The experimental system is designed to load a sample loop with a desired gas mixture, which at a given time can be released into a feeder stream as a pulse through the flow cell. The flow cell consists of an air dried 98cm x 3.6cm core of the Fell Sandstone surrounded by aluminium foil and treated with epoxy resin to provide air tight stable conditions. The core is encased upstream and downstream by gas dispersion plates to allow unobstructed gas flow. Real-time analysis of the arrival peaks of the gases downstream is recorded using a HPR20-QIC Quadrupole Mass Spectrometer (QMS).

5.2. Noble Gas and CO₂ Pulse Experiments

He and Ar pulses have been flowed through a CO₂ carrier gas and the arrival profiles measured (Fig 6). The peak arrival times of Ar were similar to that of He; however, and significantly, He arrival was marginally slower at each pressure. The differences in peak arrival times between the He and Ar curves increased as the pressure decreased and the curve profiles for the two noble gases systems differ greatly. The Ar curve profiles also show a steeper angle for initial appearance, but have a longer tail than the He curves do. The CO₂ pulses were passed through a N₂ carrier gas. The CO₂ pulses yield slower peak arrival times compared to those of both He and Ar (Fig. 6).

These results are significantly different from the curves predicted by modelling with the arrival times of all gases in the flow experiments being an order of magnitude faster than models predict. Additionally modelling predicts that He should appear the quickest out of the three gas mixtures and it should have had the best retention of the three gases. However, He takes longer to arrive than Ar and exhibits a shorter duration peak. This is because the current

standard modelling techniques do not account for any dispersion taking place. It is clear that that this process is greatly affecting the time it takes the gases to reach the sampling point downstream. He is susceptible to routes that a larger molecule such as CO_2 would be too large to pass through. As a result current model will tend to overestimate the transport rates of the noble gases through the porous media.

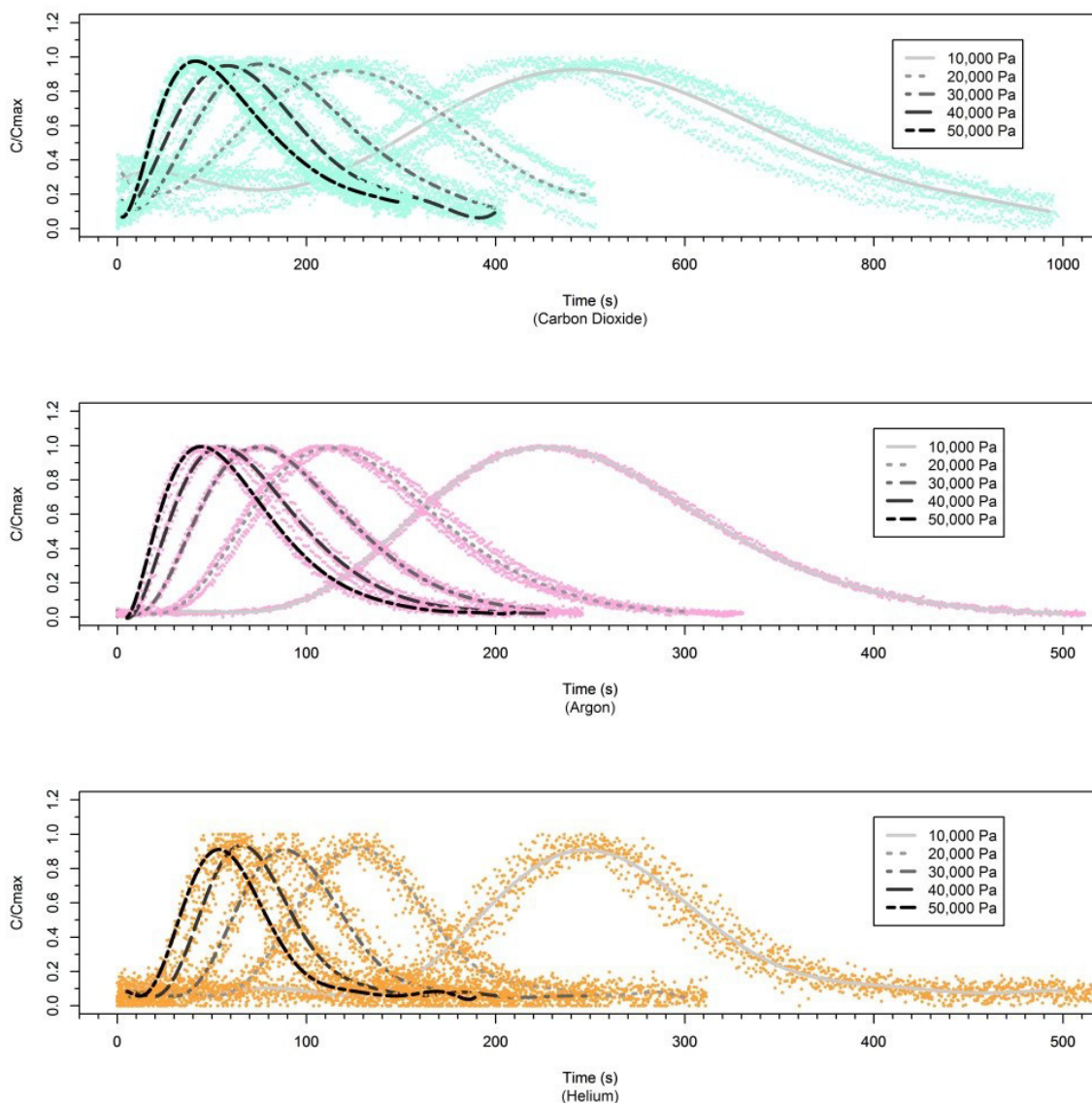


Fig. 6. Experimental results of flow experiments through the flow cell. Experiments were carried out over five different pressures. Each experiment was replicated five times. Results are plotted as scatter plots (cyan for CO_2 , pink for argon, orange for helium). Regression lines have been plotted to represent the relationship between the gas concentrations (C/C_{\max}) over time (s) as an average of the five experiments.

This preliminary data is the first step in determining how the travel times of CO_2 , He and Ar behave relative to each other in porous media. It is our intention to expand this research to the remainder of the noble gases (excluding

Rn). As shown in these early results, the noble gases may be susceptible to enter smaller pore spaces routes that a CO₂ molecule is too large to pass through. Partitioning of the noble gases between the CO₂ and other phases present will also occur – this will need to be considered. Upscaling of these results will determine how effective the different noble gases could be at acting as early warning tracers of CO₂ migration within and out with real world storage sites.

6. Summary and Conclusions

The work documented here illustrates that good progress has been made in using noble gases in tracing the origin, migration and fate of both natural and anthropogenic CO₂. Given the breadth of the applications of noble gases in CO₂ storage and monitoring it is imperative that the progress made in this field is continued. It is therefore essential that future pilot and early industrial scale CO₂ injection studies continue to investigate the behaviour of noble gases in the subsurface in order to help develop suitable noble gas monitoring strategies for universal deployment in the future.

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